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13. ABSTRACT (Maximum 200 words)

New organic amphphiles were designed with cross-sectional shapes designed for the formation of crystalline monolayers that would conform to heretofore undiscovered two dimensional packings. The viability of the molecules was tested by atom-atom potential calculations. Those systems that were deemed promising for formation of new crystalline monolayers were subsequently synthesized thereby creating new types of amphiphiles. Further examination of the crystalline monolayers was provided by determination of surface istherms and atomic force microscopy. A racemic mixture of a tetracyclic alcohol was shown to undergo chiral phase separation upon transfer to a mica substrate. A trinorborance derivative showed , within experimental error, the first static hexagonal packing of a monolayer. Molecules based on the tetracyclic alcohol exhibited surface pressures approaching that of water. These films do not appear to collapse at ambient temperature but demonstrate a hysteretic return to nearly the original low pressure areas after collapse.

14. SUBJECT TERMS
Langmuir films, organic monolayers, two-dimensional crystals, molecular packing

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A. Statement of Problem Studied

The object of this research was to devise amphiphilic molecules that would pack reliably into two-dimensional arrangements that could be exploited for use as nanostructured materials. The goal is essentially to achieve synthesis of two-dimensional supramolecules. To accomplish this, the amphiphiles were considered to be tripartite with a packing domain, a sensor domain, and a surface domain. Crucial to the research is the creation of a packing domain that can provide the underlying structural template and stability for the more active and responsive parts of the molecule. The problem of packing of molecules in three-dimensions remains one of great difficulty but this is decreased by better than an order of magnitude when considered in two dimensions. Thus, the amphiphiles to be designed exploit the cross-sectional area of the molecule created by a part of extreme rigidity. Upon this foundation groups are place which are responsive to their environment. Just as the packing dictates the material behavior of three dimensional crystals, so it is with those in two dimensions. The problem is then to control the packing and to obtain suitable behavior to justify the system as a nanoscale device.

B. Summary of Results and Achievements

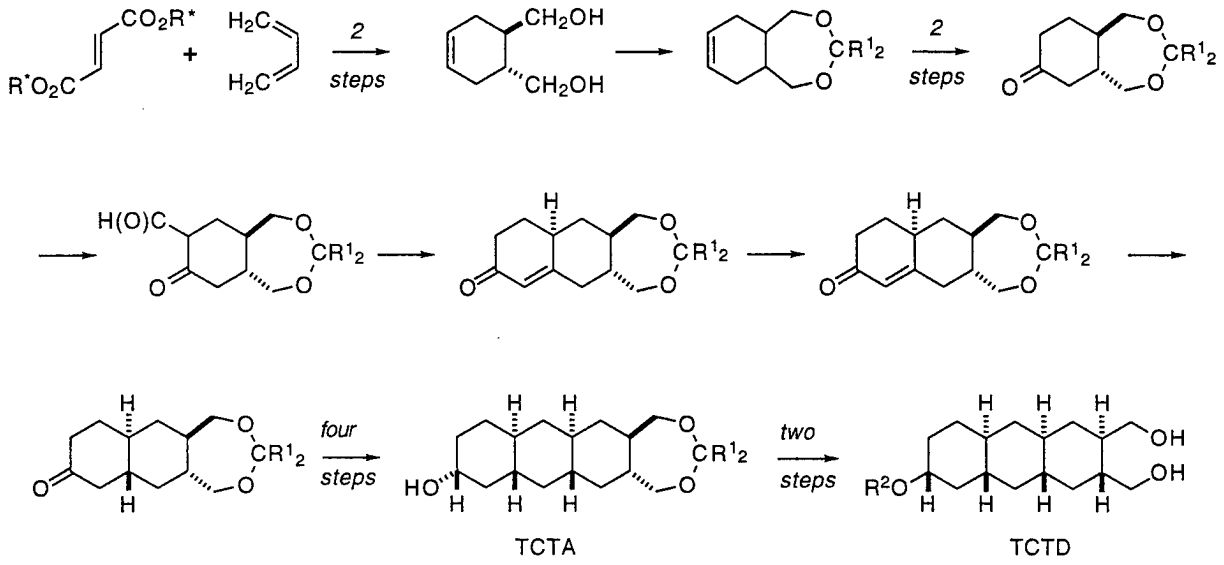
The research was divided into two critical and highly interdependent parts: the synthetic and the physical characterization. The synthetic agenda was quite challenging and while it was underway, effort was directed to improvement and creation of instrumentation. This involved incorporating a new, higher resolution scanning head for the atomic force microscope (AFM), the obtaining and adapting of a rectangular Langmuir trough which was to be adapted for Brewster angle microscopy (BAM).

The new atomic force microscope head was the Discoverer head made by Topometrix. This purchase was made for consistency with our then exisiting Topometrix system. Unfortunately, the Discoverer head was quite unstable and proved very unreliable for the promised molecular resolution. A great deal of time and effort was expended, to the extent of relocation of the instrument in a new laboratory, to obtain reasonable results. These were finally achieved although never to the quality desired. Nevertheless, the instrument did prove itself an excellent friction force microscope.

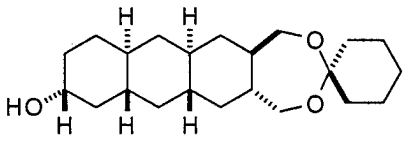
Lack of observation of the behavior of the monolayer films in the mesoscopic regime prompted design and fabrication of a Brewster angle microscope. This instrument was built of components available in our laboratory, save for the HeNe laser, after careful design such that surface isotherms could be accurately measured during the imaging. Further, significant attention was devoted to design of the instrument for digital storage and processing of the images. This required development of a program appropriate to our instrumentation. The instrument is also designed such that it can be used for surface tension measurements obtained by light scattering from surface capillary waves.

This new instrumentation has proven to be extremely flexible and useful in the study of the organic monolayers on water or mica substrate.

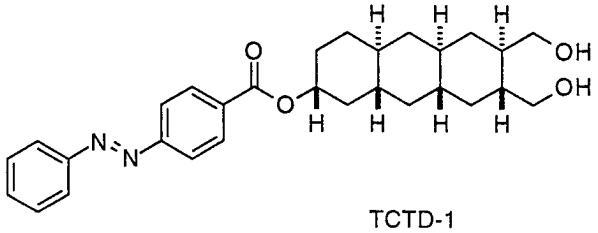
We synthesized certain chiral tricyclic triol derivatives based on the core structures shown in the alcohol TCTA and the diol TCTD. The synthesis (illustrated below) was worked out in our labs, and we were able to produce substantial laboratory quantities of these derivatives in enantiomerically pure form as either enantiomer or as the racemate as desired. The synthesis is readily amenable to the future preparation of the corresponding thiol or disulfide derivatives, and therefore, the information gained from our studies could be extended to self-assembled monolayer technology.



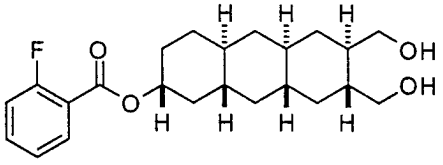
The core structures, TCTA and TCTD, permitted a great deal of flexibility for the preparation of novel amphiphiles, and in the course of our studies, we had considerable success in the preparation of novel amphiphiles. For example, the amphiphiles TCTA-1 and TCTD-1, TCTD-2, and TCTD-4 (shown below) formed well-ordered, highly stable Langmuir films.



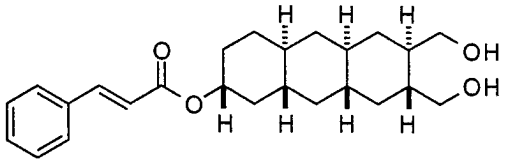
TCTA-1



TCTD-1



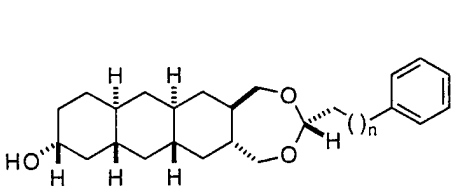
TCTD-3



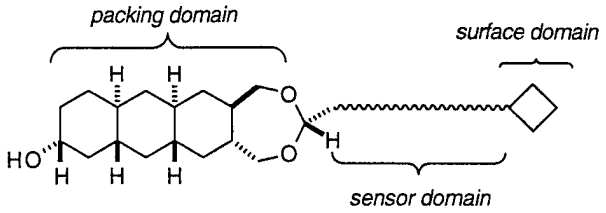
TCTD-4

Under the tenure of this grant, we also prepare derivatives of the TCTA and TCTD core to exploit surface modification and/or sensor capabilities. The idea will be illustrated for the TCTA series. We prepared the derivative TCTA-2 and -3 (shown below). These, too, form well-ordered films. Our excitement over these particular TCTA derivative derives from the fact that they represents a single amphiphile with three (independently tunable) functional domains.

The hydrophilic end will control the packing characteristics. The hydrophobic end will control the surface characteristics and the region label sensor domain will enable us to change the surface characteristics in response to a stimulus. The approach highlights certain fundamental questions; in particular, that this single amphiphile must pack in different phases for each domain. This is an important consideration since we reason the sensor domain is likely to require a more fluid environment to accommodate the molecular motion.



TCTA-2 (n = 1)
TCTA-3 (n = 8)



Unfortunately, the TCTD-1 proved unsuccessful as a light-sensitive system. The hope was that upon photoisomerization a large dipole would be induced in the acentric unit cell thus creating a ferroelectric system. While the amphiphile did form a film, it did not show any significant response to the light.

TCTA-1 formed a highly stable film that indicated that it was relatively free of defects. However, we were not able to successfully image the film for AFM study. This was attributed to the molecule's rigidity in the packing region. Unusual surface isotherm behavior was found in that at high surface pressures the film exhibited some variability in the shape of the isotherm and the onset of collapse. This is attributed to the flexibiltiy of the spiro-type ring system at the top of the molecule. The conformational lability of this part of the molecule can lead to many different packing geometries which may differ little form each other energetically. We were not able to pursue this aspect of the amphiphile's film behavior because of great variability in its packing upon transfer to a solid (mica) substrate. Attempts were made at horizontal transfer by draining the trough so the film would deposit on the substrate but this proved unsuccesful.

The TCTD-4 proved to be a more interesting system. It displayed extremely high maximum surface pressures. However, more unusual was the observation that even though a limiting pressure was reached, the film appeared to display extemely small, physically unreasonable, areas. This was observed in spite of the fact that no collapse was observed on the trough. After much observation, it was found that the film was extremely rigid, so much so that it literally slid off the water surface of the radial trough. The Brewster angle microscopy indicates that the film may aggregate at low coverages and that these islands do not fuse together as do those of the fatty acids. Rather, the islands appear to be so rigid that they ride up upon each other much as ice floes. This accounts for the compression to small areas without the collapse seen for traditional fatty acid amphiphiles. Upon release of tension, the floes are drawn back into the water and the original area is returned, or almost so. The discrepancy is attributed to some debris remaining behind. It was posited that the molecules are so rigid because the phenyl "cap" on adjacent molecules overlay each other such that a covalent bond would have to be broken to cause film collapse. This explains the strength of the film even though the limiting surface pressures are not exceptionally high. The surface isotherms only gage the lateral

interactions and do not account for the inhibition of collapse due to the capping groups.

The TCTD-3 forms films with behaviors much like those of TCTD-4. Of course, this molecule has a large dipole moment at its "surface" which, given the chiral nature of the molecule, should lead to packing in an acentric two dimensional lattice. The result of this should be a net polarization in the two-dimensional unit cell with concomitant ferroelectric behavior. An apparatus to create an electric field to orient the molecules was devised but no significant ordering of the dipoles was found. Apparently, the capping arrangement locks the fluorophenyl groups into different geometries which on the mesoscopic scale average out and thus generate no ferroelectric behavior.

Greatest progress was made in theoretical and calculational understanding of the packing and phase behavior of monolayer films. We chose two approaches. One was calculational which used idealized models of molecules to understand what properties of the molecule affect the packing to form a film. The other approach was more theoretical using a mean field theory of solids to explain the phase behavior of fatty acids. These simple systems were deemed best for an initial theoretical approach since their phase behavior is well-documented. The intent was to develop a viable theory for these simpler systems before attacking the more complicated amphiphiles being synthesized under the tenure of this grant.

The calculational results first involved modeling the packing only upon the cross-sectional geometry of the molecule. This proved to be as effective as the more elaborate atom-atom potential calculations and demonstrated the cross-sectional approach was a convenient and facile way to determine if a given molecule could pack in a desired pattern. However, such a truly two-dimensional model cannot account for the tilt-phase behavior that arises due to the finite length of the amphiphile. This lead to a string of bead model for the molecule. The results of the calculations showed that the distance between beads as well as their diameter was critical to the nature of the tilt that would be exhibited by the molecules in the film. Quite simple relationships were found that can be exploited by synthetic chemists who may desire to either have or obviate tilt phases in their films.

On a more theoretical level, mean field theory of phase transitions in three dimensional solids was used to understand critical phenomena in two dimensional systems, specifically fatty acids. The common approach is to regard the monolayer films as liquids or liquid crystals. Our approach is form the other "side" and we use mean field theory to rationalized the observed phase behavior of the fatty acids. This proved to be enormously successful and, in fact, this approach explains more of the phase behavior of fatty acids than any other theoretical approach. The strength of our formulation is its general applicability and its amenability to experimental test. We hope that, in time, the advantages of this approach will be appreciated but, since it is cast in a theoretical framework unfamiliar to almost all in the field, it will take some time for it to be employed. At the conclusion of the grant period, we had devised an approach which would also describe in a consistent way the liquid and gas phase behavior of the fatty acid monolayers thereby generating the first theory that provides an effective model for *all* the observed phases of the fatty acid monolayers on water.

C. List of Publications

"Monte Carlo Calculations of Non-tilt Phase Transitions in a Langmuir Monolayer using Cross Section Potentials," *J. Chem. Phys.*, **99**, 8194-8199 (1993), D. R. Swanson, R. J. Hardy and C. J. Eckhardt.

"Crystal Engineering in Two Dimensions: Control of Planar Packing by Design of New Amphiphiles," *Thin Solid Films*, **242**, 67-73 (1994), N. M. Peachey, D. R. Swanson, P. Dussault, J. Takacs, P. Beak, R. A. Uphaus and C. J. Eckhardt.

"Cross-section Potentials for Calculation of Close-Packing Geometries of Monolayer Films," *Thin Solid Films*, **244**, 824-826 (1994), D. R. Swanson, R. J. Hardy, and C. J. Eckhardt.

"Structural Studies of Ordered Monolayers using Atomic Force Microscopy," *Micron*, **25**, 271-292 (1994), N. M. Peachey and C. J. Eckhadt. [**Invited review article**.]

"Phase Transitions in Quasi-Two-Dimensional Molecular Solids: A Microscopic Theory of Tilt and Structural Instabilities in Langmuir Monolayers," *J. Phys. Chem.*, **99**, 8872-8887 (1995), T. Luty and C. J. Eckhardt.

"Model Calculations of Langmuir Monolayers: Pressure Effects on Tilting Behavior of Idealized Amphiphiles," *J. Chem. Phys.*, **105**, 673-677 (1996), D. R. Swanson, R. J. Hardy, and C. J. Eckhardt.

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		Harry Garcia
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		David Pugmire
		Chris Sanstedt
		Jon Selbo
		Jeff Atkins
DAAH04-93-G-0159		
		Sal Bonafede
		Alex Moser
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		John Selbo
		Summer Darling*

E. Report of Inventions. None